

## 8.1: Solutions and their Concentrations

### Learning Objectives

Make sure you thoroughly understand the following essential ideas:

- Describe the major reasons that solutions are so important in the *practical* aspects of chemistry.
- Explain why expressing a concentration as "x-percent" can be ambiguous.
- Explain why the molarity of a solution will vary with its temperature, whereas molality and mole fraction do not.
- Given the necessary data, convert (in either direction) between any two concentration units, e.g. molarity - mole fraction.
- Show how one can prepare a given volume of a solution of a certain molarity, molality, or percent concentration from a solution that is more concentrated (expressed in the same units.)
- Calculate the concentration of a solution prepared by mixing given volumes to two solutions whose concentrations are expressed in the same units.

Solutions are *homogeneous* (single-phase) mixtures of two or more *components*. For convenience, we often refer to the majority component as the *solvent*; minority components are *solutes*; there is really no fundamental distinction between them. Solutions play a very important role in Chemistry because they allow intimate and varied encounters between molecules of different kinds, a condition that is essential for rapid chemical reactions to occur. Several more explicit reasons can be cited for devoting a significant amount of effort to the subject of solutions:

- For the reason stated above, most chemical reactions that are carried out in the laboratory and in industry, and that occur in living organisms, take place in solution.
- Solutions are so common; very few pure substances are found in nature.
- Solutions provide a convenient and accurate means of introducing known small amounts of a substance to a reaction system. Advantage is taken of this in the process of titration, for example.
- The physical properties of solutions are sensitively influenced by the balance between the intermolecular forces of like and unlike (solvent and solute) molecules. The physical properties of solutions thus serve as useful experimental probes of these intermolecular forces.

We usually think of a solution as a liquid made by adding a gas, a solid or another liquid *solute* in a liquid *solvent*. Actually, solutions can exist as gases and solids as well.

Solid solutions are very common; most natural minerals and many metallic alloys are solid solutions.

Still, it is liquid solutions that we most frequently encounter and must deal with. Experience has taught us that sugar and salt dissolve readily in water, but that "oil and water don't mix". Actually, this is not strictly correct, since all substances have at least a slight tendency to dissolve in each other. This raises two important and related questions: why do solutions tend to form in the first place, and what factors limit their mutual solubilities?

### Understanding Concentrations

*Concentration* is a general term that expresses the quantity of solute contained in a given amount of solution. Various ways of expressing concentration are in use; the choice is usually a matter of convenience in a particular application. You should become familiar with all of them.

#### Parts-per concentration

In the consumer and industrial world, the most common method of expressing the concentration is based on the quantity of solute in a fixed quantity of solution. The "quantities" referred to here can be expressed in weight, in volume, or both (i.e., the *weight* of solute in a given *volume* of solution.) In order to distinguish among these possibilities, the abbreviations (w/w), (v/v) and (w/v) are used.

In most applied fields of Chemistry, (w/w) measure is often used, and is commonly expressed as weight-percent concentration, or simply "percent concentration". For example, a solution made by dissolving 10 g of salt with 200 g of water contains "1 part of salt per 20 g of water".

"Cent" is the Latin-derived prefix relating to the number 100 (L. *centum*), as in *century* or *centennial*. It also denotes 1/100th (from L. *centesimus*) as in *centimeter* and the monetary unit *cent*. It is usually more convenient to express such concentrations as "parts

per 100", which we all know as "percent". So the solution described above is a "5% (w/w) solution" of NaCl in water. In clinical chemistry, (w/v) is commonly used, with weight expressed in grams and volume in mL (Example 8.1.1).

#### ✓ Example 8.1.1

The normal saline solution used in medicine for nasal irrigation, wound cleaning and intravenous drips is a 0.91% (w/v) solution of sodium chloride in water. How would you prepare 1.5 L of this solution?

##### **Solution**

The solution will contain 0.91 g of NaCl in 100 mL of water, or 9.1 g in 1 L. Thus you will add  $(1.5 \times 9.1\text{g}) = 13.6\text{ g}$  of NaCl to 1.5 L of water.

Percent means parts per 100; we can also use parts per thousand (ppt) for expressing concentrations in grams of solute per kilogram of solution. For more dilute solutions, parts per million (ppm) and parts per billion ( $10^9$ ; ppb) are used. These terms are widely employed to express the amounts of trace pollutants in the environment.

#### ✓ Example 8.1.2

Describe how you would prepare 30 g of a 20 percent (w/w) solution of KCl in water.

##### **Solution**

The weight of potassium chloride required is 20% of the total weight of the solution, or  $0.2 \times (30\text{ g}) = 6.0\text{ g}$  of KCl. The remainder of the solution ( $30 - 6 = 24$ ) g consists of water. Thus you would dissolve 6.0 g of KCl in 24 g of water.

#### Weight/volume and volume/volume basis

It is sometimes convenient to base concentration on a fixed volume, either of the solution itself, or of the solvent alone. In most instances, a 5% by volume solution of a solid will mean 5 g of the solute dissolved in 100 ml of the solvent.

#### ✓ Example 8.1.3

Fish, like all animals, need a supply of oxygen, which they obtain from oxygen dissolved in the water. The minimum oxygen concentration needed to support most fish is around 5 ppm (w/v). How many moles of  $\text{O}_2$  per liter of water does this correspond to?

##### **Solution**

5 ppm (w/v) means 5 grams of oxygen in one million mL (1000 L) of water, or 5 mg per liter. This is equivalent to  $(0.005\text{ g}) / (32.0\text{ g mol}^{-1}) = 1.6 \times 10^{-4}\text{ mol}$ .

If the solute is itself a liquid, volume/volume measure usually refers to the volume of solute contained in a fixed volume of *solution* (not *solvent*). The latter distinction is important because volumes of mixed substances are not strictly additive. These kinds of concentration measure are mostly used in commercial and industrial applications. The "proof" of an alcoholic beverage is the (v/v)-percent, multiplied by two; thus a 100-proof vodka has the same alcohol concentration as a solution made by adding sufficient water to 50 ml of alcohol to give 100 ml of solution.

#### Molarity: mole/volume basis

This is the method most used by chemists to express concentration, and it is the one most important for you to master. Molar concentration (molarity) is the number of moles of solute per liter of solution.

The important point to remember is that the volume of the *solution* is different from the volume of the *solvent*; the latter quantity can be found from the molarity only if the densities of both the solution and of the pure solvent are known. Similarly, calculation of the weight-percentage concentration from the molarity requires density information; you are expected to be able to carry out these kinds of calculations, which are covered in most texts.

#### ✓ Example 8.1.4

How would you make 120 mL of a 0.10 M solution of potassium hydroxide in water?

##### Solution

The amount of KOH required is

$$(0.120 \text{ L}) \times (0.10 \text{ mol L}^{-1}) = 0.012 \text{ mol.}$$

The molar mass of KOH is 56.1 g, so the weight of KOH required is

$$(0.012 \text{ mol}) \times (56.1 \text{ g mol}^{-1}) = 0.67 \text{ g} \quad (8.1.1)$$

We would dissolve this weight of KOH in a volume of water that is less than 120 mL, and then add sufficient water to bring the volume of the solution up to 120 mL.

Note: if we had simply added the KOH to 120 mL of water, the molarity of the resulting solution would not be the same. This is because volumes of different substances are not strictly additive when they are mixed. Without actually measuring the volume of the resulting solution, its molarity would not be known.

#### ✓ Example 8.1.5

Calculate the molarity of a 60-% (w/w) solution of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) in water whose density is  $0.8937 \text{ g mL}^{-1}$ .

##### Solution

One liter of this solution has a mass of 893.7 g, of which

$$0.60 \times (893.7 \text{ g}) = 536.2 \text{ g} \quad (8.1.2)$$

consists of ethanol. The molecular weight of  $\text{C}_2\text{H}_5\text{OH}$  is 46.0, so the number of moles of ethanol present in one liter (that is, the molarity) will be

$$\frac{536.2 \text{ g}}{\frac{46.0 \text{ g mol}^{-1}}{1 \text{ L}}} = 11.6 \text{ mol L}^{-1} \quad (8.1.3)$$

### Normality and Equivalents

*Normality* is a now-obsolete concentration measure based on the number of *equivalents* per liter of solution. Although the latter term is now also officially obsolete, it still finds some use in clinical- and environmental chemistry and in electrochemistry. Both terms are widely encountered in pre-1970 textbooks and articles.

The *equivalent weight* of an *acid* is its molecular weight divided by the number of titratable hydrogens it carries. Thus for sulfuric acid  $\text{H}_2\text{SO}_4$ , one mole has a mass of 98 g, but because both hydrogens can be neutralized by strong base, its equivalent weight is  $98/2 = 49 \text{ g}$ . A solution of 49 g of  $\text{H}_2\text{SO}_4$  per liter of water is 0.5 molar, but also "1 normal" ( $1N = 1 \text{ eq/L}$ ). Such a solution is "equivalent" to a 1M solution of HCl in the sense that each can be neutralized by 1 mol of strong base.

solution of  $\text{FeCl}_3$  is said to be "3 normal" (3 N) because it dissociates into three moles/L of chloride ions.

Although molar concentration is widely employed, it suffers from one serious defect: since volumes are temperature-dependent (substances expand on heating), so are molarities; a 0.100 M solution at  $0^\circ \text{C}$  will have a smaller concentration at  $50^\circ \text{C}$ . For this reason, molarity is not the preferred concentration measure in applications where physical properties of solutions and the effect of temperature on these properties is of importance.

### Mole fraction: mole/mole basis

This is the most fundamental of all methods of concentration measure, since it makes no assumptions at all about volumes. The mole fraction of substance  $i$  in a mixture is defined as

$$X_i = \frac{n_i}{\sum_j n_j} \quad (8.1.4)$$

in which  $n_j$  is the number of moles of substance  $j$ , and the summation is over all substances in the solution. Mole fractions run from zero (substance not present) to unity (the pure substance). The sum of all mole fractions in a solution is, by definition, unity:

$$\sum_i X_i = 1 \quad (8.1.5)$$

#### ✓ Example 8.1.6

What fraction of the molecules in a 60-% (w/w) solution of ethanol in water consist of  $\text{H}_2\text{O}$ ?

##### Solution

From the previous problem, we know that one liter of this solution contains 536.2 g (11.6 mol) of  $\text{C}_2\text{H}_5\text{OH}$ . The number of moles of  $\text{H}_2\text{O}$  is

$$(893.7 - 536.2) \text{ g} / (18.0 \text{ g mol}^{-1}) = 19.9 \text{ mol.}$$

The mole fraction of water is thus

$$\frac{19.9}{19.9 + 11.6} = 0.63 \quad (8.1.6)$$

Thus 63% of the molecules in this solution consist of water, and 37% are ethanol.

In the case of ionic solutions, each kind of ion acts as a separate component.

#### ✓ Example 8.1.7

Find the mole fraction of water in a solution prepared by dissolving 4.5 g of  $\text{CaBr}_2$  in 84.0 mL of water.

##### Solution

The molar mass of  $\text{CaBr}_2$  is 200 g, and 84.0 mL of  $\text{H}_2\text{O}$  has a mass of very close to 84.0 g at its assumed density of  $1.00 \text{ g mL}^{-1}$ . Thus the number of moles of  $\text{CaBr}_2$  in the solution is

$$\frac{4.50 \text{ g}}{200 \text{ g/mol}} = 0.0225 \text{ mol} \quad (8.1.7)$$

Because this salt is completely dissociated in solution, the solution will contain 0.268 mol of  $\text{Ca}^{2+}$  and  $(2 \times .268) = 0.536$  of  $\text{Br}^-$ . The number of moles of water is

$$(84 \text{ g}) / (18 \text{ g mol}^{-1}) = 4.67 \text{ mol.}$$

The mole fraction of water is then

$$\frac{0.467 \text{ mol}}{0.268 + 0.536 + 4.67 \text{ mol}} = \frac{0.467}{5.47} = 0.854 \quad (8.1.8)$$

Thus  $\text{H}_2\text{O}$  constitutes 85 out of every 100 molecules in the solution.

### Molality: mole/weight basis

A 1-molal solution contains one mole of solute per 1 kg of solvent. Molality is a hybrid concentration unit, retaining the convenience of mole measure for the solute, but expressing it in relation to a temperature-independent mass rather than a volume. Molality, like mole fraction, is used in applications dealing with certain physical properties of solutions; we will see some of these in the next lesson.

#### ✓ Example 8.1.8

Calculate the molality of a 60-% (w/w) solution of ethanol in water.

##### Solution

From the above problems, we know that one liter of this solution contains 11.6 mol of ethanol in

$$(893.7 - 536.2) = 357.5 \text{ g}$$

of water. The molarity of ethanol in the solution is therefore

$$(11.6 \text{ mol}) / (0.3575 \text{ kg}) = 32.4 \text{ mol kg}^{-1}.$$

## Conversion between Concentration Measures

Anyone doing practical chemistry must be able to convert one kind of concentration measure into another. The important point to remember is that any conversion involving molarity requires a knowledge of the *density* of the solution.

### ✓ Example 8.1.9

A solution prepared by dissolving 66.0 g of urea  $(\text{NH}_2)_2\text{CO}$  in 950 g of water had a density of  $1.018 \text{ g mL}^{-1}$ . Express the concentration of urea in

- weight-percent
- mole fraction
- molarity
- molality

#### Solution

a) The weight-percent of solute is  $(100\%)^{-1} (66.0 \text{ g}) / (950 \text{ g}) = 6.9\%$

The molar mass of urea is 60, so the number of moles is

$$(66 \text{ g}) / (60 \text{ g mol}^{-1}) = 1.1 \text{ mol}.$$

The number of moles of  $\text{H}_2\text{O}$  is

$$(950 \text{ g}) / (18 \text{ g mol}^{-1}) = 52.8 \text{ mol}.$$

b) Mole fraction of urea:

$$(1.1 \text{ mol}) / (1.1 + 52.8 \text{ mol}) = 0.020$$

c) molarity of urea: the volume of 1 L of solution is

$$(66 + 950) \text{ g} / (1018 \text{ g L}^{-1}) = 998 \text{ mL}.$$

The number of moles of urea (from a) is 1.1 mol.

Its molarity is then

$$(1.1 \text{ mol}) / (0.998 \text{ L}) = 1.1 \text{ mol L}^{-1}.$$

d) The molality of urea is  $(1.1 \text{ mol}) / (.066 + .950) \text{ kg} = 1.08 \text{ mol kg}^{-1}$ .

### ✓ Example 8.1.10

Ordinary dry air contains 21% (v/v) oxygen. About many moles of  $\text{O}_2$  can be inhaled into the lungs of a typical adult woman with a lung capacity of 4.0 L?

#### Solution

The number of molecules (and thus the number of moles) in a gas is directly proportional to its volume ([Avogadro's law](#)), so the mole fraction of  $\text{O}_2$  is 0.21. The molar volume of a gas at  $25^\circ \text{C}$  is

$$(298/273) \times 22.4 \text{ L mol}^{-1} = 24.4 \text{ L mol}^{-1}$$

so the moles of  $\text{O}_2$  in 4 L of air will be

$$(4 / 24.4) \times (0.21 \text{ mol}) \times (24.4 \text{ L mol}^{-1}) = 0.84 \text{ mol O}_2.$$

## Dilution calculations

These kinds of calculations arise frequently in both laboratory and practical applications. If you have a thorough understanding of concentration definitions, they are easily tackled. The most important things to bear in mind are

- Concentration is inversely proportional to volume;
- Molarity is expressed in  $\text{mol L}^{-1}$ , so it is usually more convenient to express volumes in liters rather than in mL;
- Use the principles of unit cancelations to determine what to divide by what.

### ✓ Example 8.1.11

Commercial hydrochloric acid is available as a 10.17 molar solution. How would you use this to prepare 500 mL of a 4.00 molar solution?

#### Solution

The desired solution requires  $(0.50 \text{ L}) \times (4.00 \text{ M L}^{-1}) = 2.0 \text{ mol}$  of HCl. This quantity of HCl is contained in  $(2.0 \text{ mol}) / (10.17 \text{ M L}^{-1}) = 0.197 \text{ L}$  of the concentrated acid. So one would measure out 197 mL of the concentrated acid, and then add water to make the total volume of 500 mL.

### ✓ Example 8.1.12

Calculate the molarity of the solution produced by adding 120 mL of 6.0 M HCl to 150 mL of 0.15 M HCl. What important assumption must be made here?

#### Solution

The assumption, of course, is that the density of HCl within this concentration range is constant, meaning that their volumes will be additive.

Moles of HCl in first solution:

$$(0.120 \text{ L}) \times (6.0 \text{ mol L}^{-1}) = 0.72 \text{ mol HCl}$$

Moles of HCl in second solution:

$$(0.150 \text{ L}) \times (0.15 \text{ mol L}^{-1}) = 0.02 \text{ mol HCl}$$

Molarity of mixture:

$$(0.72 + 0.02) \text{ mol} / (.120 + .150) \text{ L} = 4.3 \text{ mol L}^{-1}.$$

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